

NASA Contractor Report 3696

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Experiments With Phase Transitions at Very High Pressure

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GRANT NAGW-8
JUNE 1983



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1958-1983

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Experiments With Phase Transitions at Very High Pressure

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Prepared for
Lewis Research Center
under Grant NAGW-8



National Aeronautics
and Space Administration

**Scientific and Technical
Information Branch**

1983

I. INTRODUCTION

The National Aeronautics and Space Administration has an interest in dense forms of hydrogen for possible use as a rocket fuel. It has been predicted that the metallic phase of hydrogen, formed by compression to pressures in excess of 1 Megabar, would have an energy content ~ 200 kJ/gm, which is 35 times that of TNT. If used as a rocket fuel, the propellant could amount to only ~ 20 percent of the total weight of a rocket with orbital capability with 80 percent payload. A useful review of molecular and metallic hydrogen can be found in Ross and Shishkevich (ref. 1).

In addition to its energy content, metallic hydrogen is predicted to be a high temperature superconductor. Although theoretical estimates vary, the superconducting transition has been placed as high as room temperature. In order for this to be useful, the metallic phase must be metastable. Considerable doubts exist as to the probability of useful metastability, although schemes have been proposed for cladding with other metals. This could stabilize surface nucleation events, which would otherwise lead to catastrophic transition back to the molecular phase.

Even if metallic hydrogen is not useful for these practical purposes, study of its properties, and of compressed molecular hydrogen, is of interest to planetary science. Jupiter is believed to possess a core of metallic hydrogen, for example. In addition, hydrogen metal would be the simplest possible metal, and thus of great interest as a model substance against which to check theoretical predictions.

Our research in this area began in 1972 with a program to support the construction of a large split-sphere apparatus at NASA Lewis Research Center. Two developments changed the course of research, and led to the

present program of study. Firstly, theoretical estimates of the transition pressure to the metallic state increased from ~ 0.85 Mbar to >2 Mbar (ref. 1). Secondly, it was realized that pressures claimed experimentally in apparatus with tungsten carbide anvils were overestimated (1 Mbar was downgraded to ~ 0.3 Mbar) (ref. 2).

However, experiments were already being carried out with apparatus equipped with anvils of single crystal diamond into the pressure region above 0.5 Mbar. The diamond anvil, or window, cell revolutionized very high pressure measurements and offered a way to carry out a variety of physical property measurements on compressed solids. Accordingly, the present group began to experiment with these devices in 1974, and subsequently helped to develop techniques for X-ray, optical, and electrical measurements. At the present time, it is a routine procedure to carry out measurements to ~ 0.5 Mbar, while pressures of ~ 1 Mbar can be reached with some difficulty (most of these experiments end with diamond anvil breakage). One experiment to 1.7 Mbar has been reported (ref. 3).

The present report summarizes work carried out over a two-year period, October 1979 to April 1982. A synopsis of the state of our experiments is as follows:

- (a) Diamond cells have been constructed for use to ~ 1 Mbar.
- (b) A refrigerator for cooling diamond cells has been purchased and adapted for optical and X-ray studies between ~ 15 and 300 K.
- (c) A cryostat for superconductivity studies between ~ 1.5 and 300 K has been constructed.
- (d) Optical equipment has been constructed and adapted for fluorescence, transmission and reflectance studies. This equipment includes a facility for using a ruby fluorescence pressure measurement technique.

- (e) X-ray equipment has been adapted for use with diamond cells, enabling diffraction patterns to be detected with energy-dispersive (Si-Li detector) and position sensitive devices, as well as photographic methods.
- (f) Experimental techniques have been developed for X-ray diffraction studies using synchrotron radiation. (This will be of necessity for our imminent studies on hydrogen.)
- (g) AC susceptibility techniques have been developed for detecting superconducting transitions in high pressure phases.

Using these techniques, experiments have been conducted on three main classes of materials:

- (a) Compressed solidified gases, Xe, Ar.
- (b) Semiconductors exhibiting high pressure metallic phases (Ge, Si, GaAs,...).
- (c) Materials of interest as high temperature superconductors, Nb_3Ge , Nb_3Si , Nb_3As , $CuCl$.
- (d) Iodine, representing a molecular crystal which undergoes a gradual transition to a metallic phase.

These topics will be dealt with in greater detail in the following section.

II. EXPERIMENTAL TECHNIQUES

Several advances have been made in experimental techniques during the grant period. The following is a synopsis of the state of experimental capability at the end of the grant period.

II.1. Diamond Anvil Cells

Work is being carried out using several diamond anvil cells:

a. Basic Design

This diamond cell was already constructed at the beginning of the grant period. Its most revolutionary feature was the first use of tungsten carbide rockers, and rocker alignment adjusters. Since this cell design became the basis for subsequent designs, a description appears in reference 4.

b. Low Temperature Version (Modification I)

This cell only differed from the basic design in that construction materials were of Be-Cu, and the cell was shortened to provide less thermal mass. It was constructed to fit inside a cryostat (see Sec. II.6) and was equipped with a calibrated temperature sensor. AC susceptibility coils used with this cell are described in Sec. II.7.

c. Version for Condensed Gases (Modification II)

This diamond cell was constructed so that the anvils could be operated remotely via lever arms and cam. A description of the cell is given in reference 5. The major drawback with this cell was its bulk, making it unrealistic to carry out X-ray diffraction measurements at low temperature. A second disadvantage was the relatively large distance between the sample and X-ray entrance point. This reduces the intensity of X-ray photons at the sample when a conventional X-ray source is used ($I \propto \text{distance}^{-2}$). However, the cell can be used to advantage with synchrotron radiation.

d. Pneumatically Operated Diamond Cell (Modification III)

This cell was designed for remote operation in the synchrotron radiation hutch. With reference to Fig. 1 of reference 4, the spring stack

was replaced by a ram. The ram was designed so that it was donut-shaped, allowing radiation to pass along its axis (16° aperture to sample).

II.2. Conventional X-Ray Techniques

At the beginning of the grant period X-ray diffraction experiments could only be carried out at CSU using lengthy photographic exposures. Funds from the NASA grant were used to purchase a position-sensitive proportional detector (PSPD). Unfortunately, several problems were encountered in its use. Firstly, the multichannel analyzer had to be replaced. Funds from the National Science Foundation were obtained for this. Secondly, the detector leaked. Since expensive Xe-CH₄ gas was used, the leak problem had to be solved. Thirdly, the carbon-coated quartz filament tended to develop dead-spots at photon intensities well below the stated limit. The detector was out of commission for ~75 percent of the time. Apparently the manufacturer knew of these problems from previous experience, but has not changed the design to correct them. At the present time the detector is being modified to incorporate a metal filament, eliminating the problem of dead spots, increasing linearity and precision, and allowing much higher photon count rates to be accommodated. The problem of leaks will be corrected using a different housing design.

An energy-dispersive [Si(Li)] detector was also purchased from the NSF grant. Preliminary measurements indicated that a different X-ray tube was needed from the Mo tube used in order to provide an energy window from ~5 to 50 keV without characteristic lines. A diffractometer (GE XRD5) with two tungsten tubes was obtained as a gift from Johns Manville Company, and work was in progress to set it up with the diamond cells at the end of the grant period.

These preliminary measurements showed, however, that even with the Mo target, the Si(Li) detector was of use in aligning the X-ray beam onto the sample. The problem can be understood simply from Fig. 1. X-rays from the tube exit via a slit, then pass through a collimator tube and the lead pin-hole collimator, onto the sample. The alignment of the pinhole (100 μm diameter) and sample (~150 μm diameter) could only be done crudely. A new collimator tube was constructed for Mod. I diamond cell, and four screws arranged in the piston, so that the pinhole could be translated in two orthogonal directions. Preliminary alignment was carried out optically, before the sample was loaded. Final alignment was then carried out with the cell in position on the X-ray apparatus. Fluorescence lines from sample and gasket were monitored, enabling the pinhole to be shifted into the optimum position.

The NSF equipment grant was also used to purchase a small computer, so that diffraction information could be directly processed from the MCA. A schematic of the present experimental arrangement is given in Fig. 2.

II.3. Synchrotron Radiation Studies

The major problem of making X-ray diffraction experiments in the diamond anvil cell arises from the great length of time needed to obtain suitable diffracted photon intensities. This problem becomes more acute as the atomic number of the sample under investigation becomes smaller. In earlier work, our group, together with E. F. Skelton from the Naval Research Laboratory, pioneered the use of Si(Li) energy dispersive detectors with diamond cells and conventional X-ray sources. It was realized that further improvements could be made by increasing the intensity of incident radiation

using photons from a synchrotron source. This source is particularly suitable for energy-dispersive analyses because of the wide range of photon energies, and the well-defined intensity-energy spectrum, and polarization.

A system has been tested at Stanford Synchrotron Laboratory, partly using NASA and ONR funding. It was found that diffraction peaks could be obtained in the wide energy range of ~5 to 50 keV. Diffraction information could be obtained in some cases in less than 10 sec. Strong advantages accrue from the wide energy range and well defined intensity spectrum, so that many diffraction peaks can be observed, and structural information obtained with higher statistical certainty.

Although earlier measurements were made by us at the Stanford Synchrotron facility (SPEAR) all subsequent measurements will be made at the Cornell facility (CHESS) because of the more advantageous spectrum. Papers have been prepared describing this technique (refs. 6, 7 and 8).

From this previous work it is apparent that a remotely operated shutter mechanism is required to collimate the incident radiation. Manually operated collimators, described in the previous section, are difficult to align in the radiation hutch. A new design for remotely operated shutters has been designed as part of the continuation grant. Development of these techniques is extremely important to our planned measurements of X-ray diffraction from compressed, solid hydrogen.

II.4. Pressure Measurement

Two techniques are used by us for pressure measurement. Firstly, an X-ray diffraction method is convenient for synchrotron studies, and sometimes when conventional X-ray measurements are being carried out. A

calibration substance is placed in the cell, together with the sample under investigation. NaCl is conveniently used for pressures up to 300 kbar (refs. 9 and 10) and MgO (ref. 11), or Au (ref. 12) for pressures to 1 Mbar.

At the beginning of the grant period, a film camera was developed with two films exactly parallel, 30 mm apart. The camera is placed ~70 mm from the sample. With this arrangement the sample-to-film distance can be obtained, thus eliminating the largest uncertainty arising from single-film measurements. Using NaCl as the pressure calibrant, the change in d-spacing can be determined to an accuracy $\Delta d/d_0 \sim \pm 0.0002$, corresponding to an accuracy in pressure of $\sim \pm 0.5$ kbar. Using stiffer materials such as MgO, the pressure uncertainty increases, for the same uncertainty in $\Delta d/d_0$.

It was found that similar accuracy could be obtained using the position-sensitive detector. The main advantages of the PSPD are the substantially shorter time period needed for data collection (~10 percent of that required for photographic techniques) and the convenience of electronic output for analysis.

Secondly, the shift of ruby fluorescence peaks with pressure is used by us for pressure measurements (refs. 13, 14, and 15). In order that the optical system be as flexible as possible for other measurements, the design illustrated in Fig. 3 was developed.

The incident laser beam is reflected from a dichroic mirror and focused by the reflecting objective onto the ruby chip inside the diamond cell. Fluorescence radiation then passes through the objective, dichroic mirror, into the eyepiece, which may be bypassed so that focussing occurs on the slit of the monochromator. A simple 0.2 m monochromator is used with an echelle grating (300 lines/mm) operating in the 7th order of diffraction. A photomultiplier tube with GaAs element is used to measure light output. The

GaAs element is thermo-electrically cooled in order to reduce noise.

A typical wavelength scan takes less than one minute, with electrical output recorded on an X-Y recorder. Instrumental accuracy of pressure measurement corresponds to <0.5 kbar. At higher pressure, the accuracy is reduced, due to the broadening of the fluorescence lines resulting from nonhydrostatic stresses. Current work is aimed at using condensed helium as the pressure transmitting medium (ref. 16) (wherever appropriate) to reduce these nonhydrostatic stresses.

II.5. Optical Measurement Procedures

The optical bench can be modified to measure the optical absorption and reflectivity of samples in the diamond cell. The arrangements were based on those of Welber (ref. 17) and are sketched in Figs. 4(a) and (b).

Measurements of time-resolved fluorescence spectroscopy were also carried out in the laboratory of Prof. Powell at Oklahoma State University (ref. 18). This is only one of the many techniques that have been added to the list of those which can be carried out in the diamond anvil cell, illustrating its versatility.

The condensed gas solids such as Xe, Ar, H₂, have very large band gaps at normal pressures, and the band gaps do not decrease below the diamond "window" at ~5 eV until fairly high pressures are reached. Accordingly, calculations were made to assess whether these band gaps could be measured using two-photon absorption techniques. It was found that experiments would only be feasible with very powerful lasers. Experiments were carried out at CSU, confirming that it was not possible to use this technique with available facilities.

II.6. Cryogenic Equipment

A variable temperature cryostat for cooling diamond cells between ~1.5 to 300 K is illustrated in Fig. 5. The diamond cell is held at the end of a shaft in the central chamber. Cooling is effected by passing cooled gas through the bottom of this central chamber, past the diamond cell. Temperature control is obtained by pre-heating this gas to the desired temperature using a heater and GaAs temperature sensing diode, controlled by a Princeton Applied Research Company Model 152 Temperature Controller. Pre-cooling may be speeded up using liquid N₂ or He poured into the central chamber. These liquids can also be used to immerse the diamond cell, so that temperatures between ~1.5 and 4 K can be obtained by pumping on liquid helium.

In order to carry out X-ray diffraction and optical measurements between ~10 and 300 K, a closed-cycle refrigerator was purchased (Air Products Model Displex DE-202). At the end of the grant period, modified tails were being constructed to enable diamond cells to be fitted into the refrigerator. A simple cooling box, enabling diamond cell Modification II to be cooled to 77 K, was also constructed. The procedure for loading compressed gas into the cell is described in reference 5.

II.7. AC Susceptibility Technique

A preliminary account of the technique, based on work performed before this grant period, is given in reference 5. This earlier method utilized a small gasket with coils surrounding it. It was found that gasket rupture occurred frequently for pressures above ~100 kbar, so that an alternative

design was developed in the current grant period, in which a large gasket diameter was used.

It was found that reasonable sensitivity could be obtained with coils wound on only one face. It was also determined that the susceptibility coils could detect a semiconductor-to-metal transition. (The imaginary component of the susceptibility, X'' , is proportional to the conductivity). The experiment was carried out on InSb, with pressure increased slowly through the transition at ~23 kbar, using the pneumatically driven cell (Mod. III).

The relatively small change in response, and the relatively large noise level (presumably caused by deformation of the gasket) do not make this an attractive method of determining nonconducting-to-conducting state transitions.

III. EXPERIMENTS

Before detailing individual experiments which have been carried out, it will be mentioned that substances investigated fall into three main categories: (a) condensed gases (Xe, Ar, I₂), (b) materials of interest as high temperature superconductors (Nb₃Ge, CuCl), and (c) semiconductors exhibiting transitions to metallic states (Ge, Si, GaAs, InSb).

III.1. Xenon

A preliminary experiment was carried out on Xe in cell Mod. II. Pressure was measured with the ruby fluorescence technique. It was

estimated that the maximum pressure reached was 450 kbar, where gasket failure prevented further compression. At this pressure the xenon was still transparent. This conflicts with the report of Nelson and Ruoff (ref. 19) who claimed a metallic state existed at only ~330 kbar, but is not in conflict with shock data (ref. 20) or model calculations (ref. 21). At the time that this experiment was carried out, X-ray diffraction facilities were not in operation, so that structural or volumetric data were not obtained.

III.2. Argon

Several experiments were carried out on argon to pressures of ~100 kbar using cell Mod. II. In the first experiment (see path in Fig. 6) initial compression to ~120 kbar occurred at 77 K. The cell was then warmed to room temperature. Pressure was then dropped stepwise, with diffraction data taken at each step. After analysis of the data, a phase transition was found to have occurred at ~40 kbar. It was not possible to identify the higher pressure phase (>40 kbar) but the lower pressure phase was the normal fcc structure. Several runs were then made by compressing to ~20 kbar at 77 K, warming to room temperature and compressing and decompressing to ~100 kbar. No transition was observed.

It was then decided to repeat the first experiment as closely as possible, since the high pressure phase could have been favored thermodynamically at lower temperature, persisting at higher temperature due to kinetic factors. Again, no phase transition could be found.

The recently published work of Finger, et al. (ref. 22) agrees with the conclusion that no phase transition exists below 90 kbar. It is conceivable

that a small quantity of O_2 or N_2 impurity contaminated the sample in the first run. This would tend to favor an hcp or similar structure.

This work also was hampered by a factor which must be taken into consideration in further work - the tendency of the compressed solid to form a few crystals. This makes polycrystalline X-ray techniques inapplicable. Data can be taken at higher pressure, where the crystals break up into many smaller crystals, and the reduced temperature T/T_{melting} is reduced because T_m is increased. The reduced temperature implies that diffusion rates are drastically reduced, so that the tendency for larger crystals to grow at the expense of smaller ones is correspondingly diminished.

III.3. Iodine

Iodine is a solid at room temperature and pressure, but can be considered a condensed gas. Our studies on iodine were prompted by earlier observations of Drickamer and co-workers (refs. 23, 24, and 25) who observed a continuous change into a metallic state at ~200 kbar.

X-ray studies by us were hampered by a curious observation - when iodine crystals were placed into contact with metallic gasket, they melted. Gaskets were then coated with a thin layer of parylene, a nonconducting polymer, with no evidence of melting.

A phase transition was observed at ~190 kbar to an unidentified structure. At this time, Minomura and co-workers published structural data on compressed I_2 using a position sensitive proportional detector (it was this work which convinced us of the superiority of this X-ray technique). Their original findings (ref. 26) disagreed with ours due to a mistake in their estimation of pressure. Subsequent work cleared up the discrepancy

(refs. 27, 28, and 29). The superiority of their X-ray data over ours made it undesirable to continue our study.

III.4. Nb₃Ge and Related Compounds

The A-15 compounds Nb₃Sn, V₃Si, etc., have been studied extensively as high temperature superconductors. High pressure studies were carried out, detailed in reference 30. The main purpose of this research was to compare compressibilities with particular emphasis on the possibility of synthesizing Nb₃Si in the A-15 structure. The results suggested that high pressure synthesis would favor the A-15 structure, and this conjecture has been borne out by two recent studies (refs. 31 and 32). Unfortunately, the superconducting transition temperature is well below the value of 30 K predicted theoretically.

III.5. Cuprous Chloride (CuCl)

Considerable interest was created in the physical properties of CuCl, following suggestions that it was a superconductor below ~170 K at high pressure (ref. 33). Our high pressure work investigated the structural and electrical/magnetic properties, but found no evidence for superconductivity. Evidence was put forward to suggest that partial disproportionation to CuCl₂ and Cu occurred. A detailed account of our research is given in references 34 and 35.

III.6. Germanium

It has been known for 20 years that Ge undergoes a phase transition to a metallic state at ~100 kbar (refs. 36, 37, and 38). Work was carried out by us on the high pressure structure of Ge using synchrotron radiation (ref. 8). Surprisingly, it was found that a new phase began to appear at only 40 kbar. Similar results were found using a conventional X-ray source and photographic detection. We then found a report of new phase lines appearing at only 25 kbar (ref. 39).

Unfortunately, further experiments showed that the results obtained were dependent on the particular run. After many experiments, we surmised that the presence of nonhydrostatic stresses in the sample can produce lower transition pressures from the normal diamond structure, to the β -Sn, metallic, structure. Further increase of non-hydrostatic stresses makes it possible to produce another structure at even lower pressure. Partial conversion of the sample can be explained, since only some crystallites have large non-hydrostatic stresses.

In order to prove this hypothesis, measurements are currently being carried out on samples in which (a) purely hydrostatic conditions can be guaranteed, and (b) uniaxial stresses are produced by pressing with the anvils directly onto a polycrystalline pellet.

Russian workers (ref. 40) have found that the super-conducting transition temperature jumps discontinuously from ~5 to 7 K as pressure is lowered below about 100 kbar. We surmise that this is related to the presence of two phases, and may be ascribable to an interfacial effect (metal-dielectric) proposed by Allender, Bray and Bardeen (ref. 41) but never observed to date.

These results are of general importance. It has been assumed in the literature that hydrostatic stresses are guaranteed in a diamond anvil experiment in which a powdered sample is used in a hydrostatic fluid. Our results show that bridging of particles between the anvils can produce nonhydrostatic stresses, even in the presence of a hydrostatic medium. A paper on this subject is in preparation.

III.7. Silicon

Experiments have been carried out on silicon in the high pressure metallic phase to confirm the high bulk modulus reported by us earlier which has been substantiated by analysis of shock data. Runs have been made using photographic and electronic detection techniques, with both conventional and synchrotron sources. Also a second phase transition (metallic-metallic) has been sought, without success, to above 700 kbar. Shock studies (ref. 42) indicate two transitions below 200 kbar, but this could be related to the high temperatures and nonhydrostatic stresses generated in the shocked samples. Russian workers (ref. 43) found a continuous phase change between 80 to 160 kbar, in conflict with our work. This could be caused by large uniaxial stresses in the Russian apparatus (see discussion of Ge). A publication is in preparation.

III.8. $\text{Nd}_{1-x}\text{Y}_x\text{P}_5\text{O}_{14}$ and Ruby

Neodymium pentaphosphate is a material which has potential for laser applications. The nature of fluorescence quenching is not completely understood and it was suggested that the variation of certain spectral

features, and fluorescence decay time, with pressure could help to distinguish between various models proposed. The study also helped us to develop our techniques for optical absorption and fluorescence measurements. The first time-resolved fluorescence measurements were carried out in the diamond anvil cell. The study was completed successfully, and similar measurements made on ruby (ref. 18).

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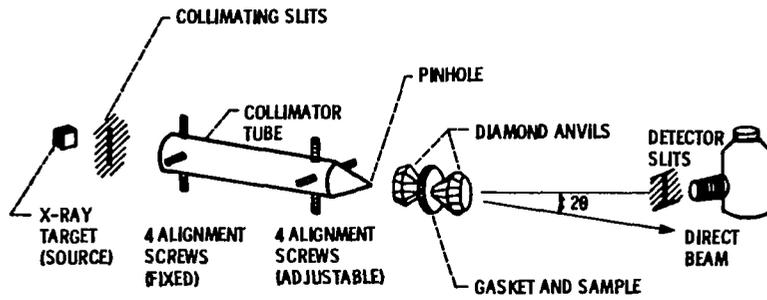


Figure 1. - Schematic of alignment system for XRD using energy-dispersive detector. (Not to scale.)

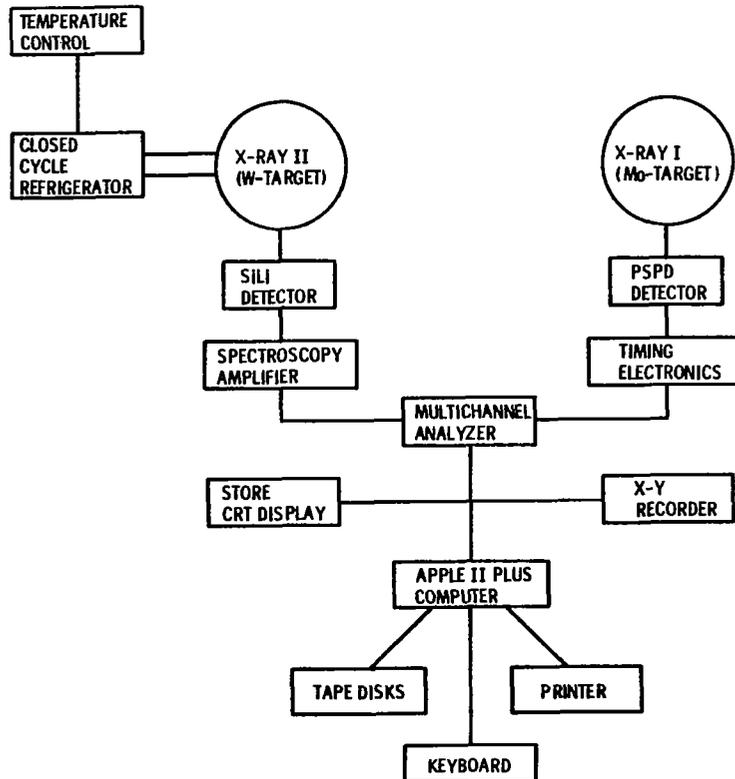


Figure 2. - Schematic of conventional-source X-ray system for high pressure measurements at CSU.

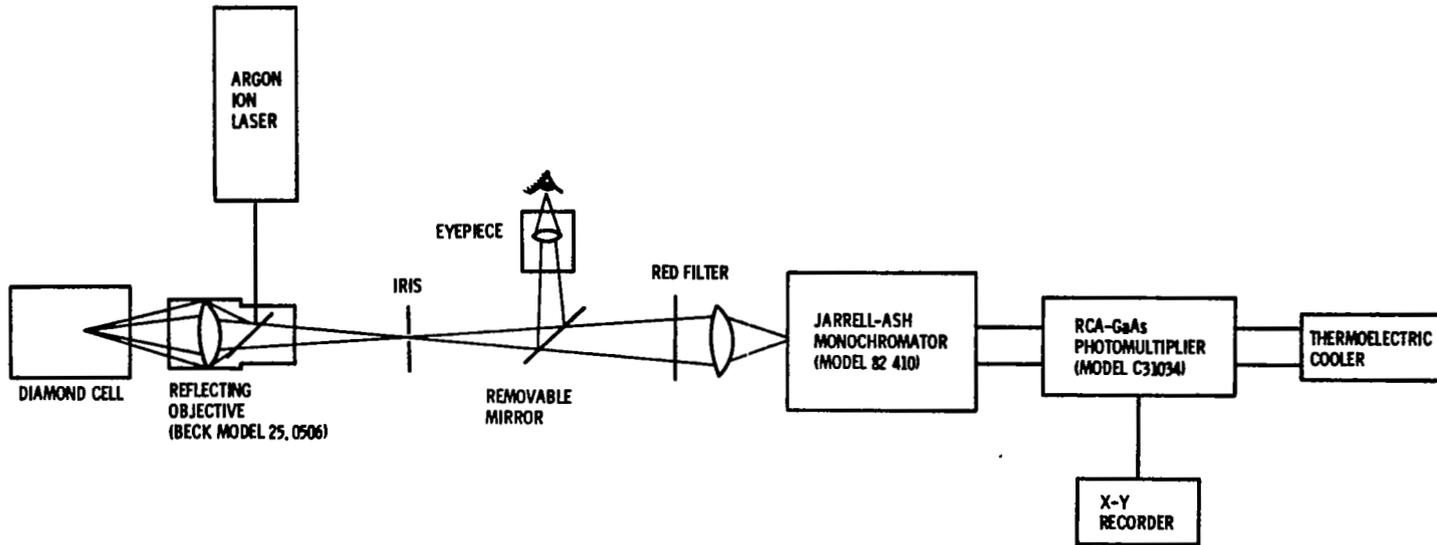


Figure 3. - Schematic of the arrangement for ruby fluorescence measurements.

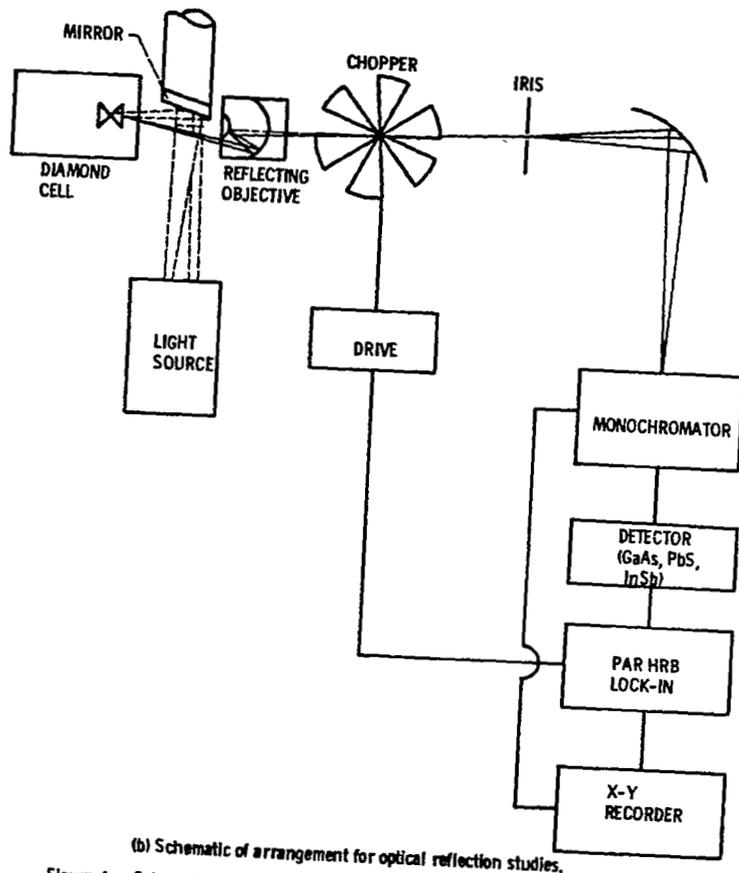
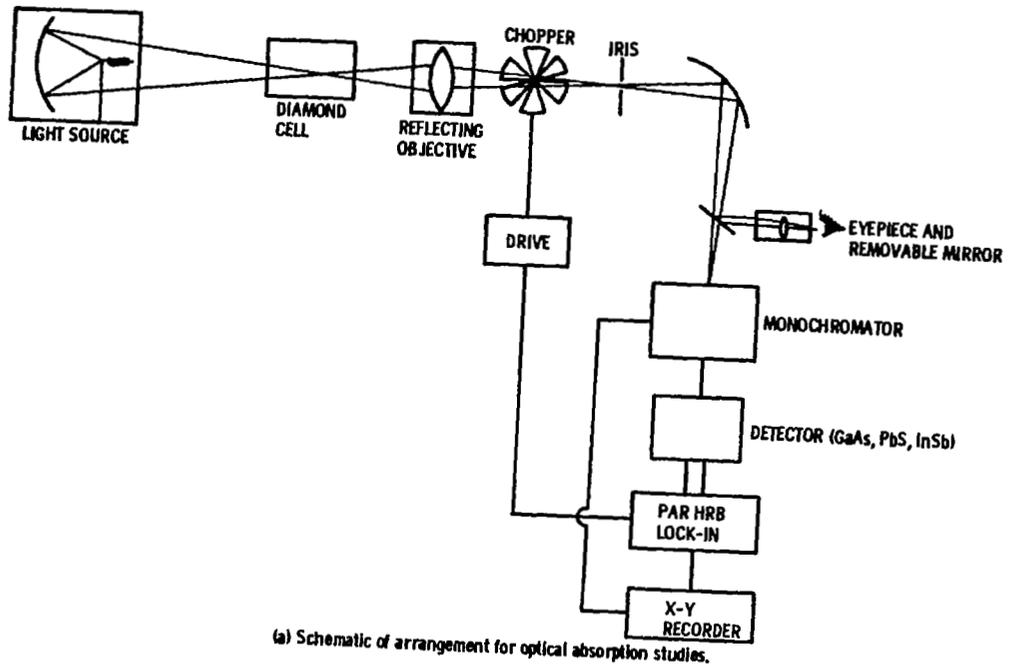


Figure 4 - Schematic arrangements for optical absorption and reflection studies.

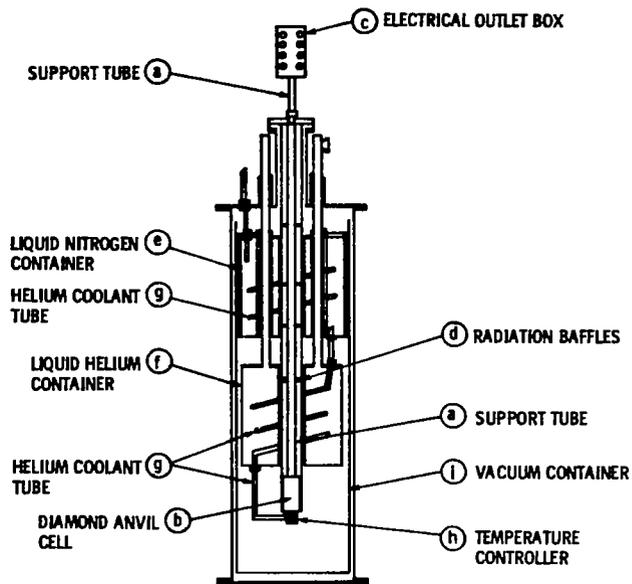


Figure 5. - Schematic of the variable temperature cryostat (~1.5 to 300 K) for cooling the diamond cells.

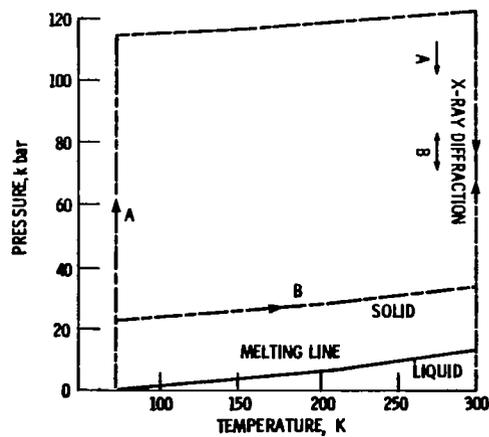


Figure 6. - Schematic showing two paths, A and B, on experiments of compressed Argon solid.

1. Report No. NASA CR-3696	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle EXPERIMENTS WITH PHASE TRANSITIONS AT VERY HIGH PRESSURE		5. Report Date June 1983	6. Performing Organization Code
		8. Performing Organization Report No. None	10. Work Unit No.
7. Author(s) Ian L. Spain		11. Contract or Grant No. NAGW-8	
9. Performing Organization Name and Address Colorado State University Dept. of Physics Fort Collins, Colorado 80523		13. Type of Report and Period Covered Contractor Report	
		14. Sponsoring Agency Code 506-56-12 (E-1513)	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546			
15. Supplementary Notes Final report. Project Manager, William R. Jones, Jr., Structures and Mechanical Technologies Division, NASA Lewis Research Center, Cleveland, Ohio 44135.			
16. Abstract This report summarizes the work performed under NASA Grant NAGW-8 from October 1979 to April 1982. Experiments with phase transitions at very high pressures were conducted. Diamond cells were constructed for use to 1 Mbar. A refrigerator for cooling diamond cells was adapted for studies between 15 and 300 K. A cryostat for superconductivity studies between 1.5 to 300 K was constructed. Optical equipment was constructed for fluorescence, transmission, and reflectance studies. X-ray equipment was adapted for use with diamond cells. Experimental techniques were developed for X-ray diffraction studies using synchrotron radiation. AC susceptibility techniques were developed for detecting superconducting transitions. The following materials were studied: compressed solidified gases (Xe, Ar), semiconductors (Ge, Si, GaAs), superconductors (Nb ₃ Ge, Nb ₃ Si, Nb ₃ As, CuCl), molecular crystals (I).			
17. Key Words (Suggested by Author(s)) High pressure physics		18. Distribution Statement Unclassified - unlimited STAR Category 76	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 29	22. Price* A03